

Influence of phenolic compounds on the $\text{Mo}(\text{CO})_6$ catalysed metathetical reactions of alkynes

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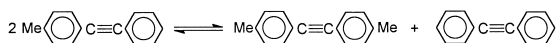
Abstract

Factors influencing the polymerisation of phenylacetylene in the presence of the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ catalytic system are not limited only to a $\text{C}_6\text{H}_5\text{OH}/\text{Mo}$ molar ratio ≥ 100 and reaction temperatures $> 110^\circ\text{C}$, but include the availability of a phenolic compound with an unassociated hydroxyl group and the use of a nonpolar solvent. In the presence of aliphatic alcohols as cocatalysts the activity of the catalytic system is greatly reduced. Terminal alkynes polymerise in the presence of the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ catalytic system at 120°C while internal alkynes undergo metathesis and/or polymerisation depending on the bulkiness of the alkyl groups attached to the triple bond. A metal carbene mechanism is supported. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Phenylacetylene; Metathetical reaction; Alkynes

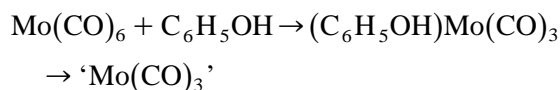
1. Introduction

The remarkable cocatalytic effect of phenol was discovered when a mixture of $\text{Mo}(\text{CO})_6$ and $\text{C}_6\text{H}_5\text{OH}$, with $\text{C}_6\text{H}_5\text{OH}$ in a large excess, metathesized *p*-tolylphenylacetylene at 110°C [1]:



Equilibrium is reached within 1 h with high selectivity [2]. Various other alkynes were also metathesized under these conditions, i.e., 2-butyne, 3-heptyne, 4-nonyne, 1-phenyl-1-butyne and 1-phenyl-1-hexyne [3].

Various theories were postulated to describe the role of phenol in the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ metathesis catalytic system. One theory suggested that phenol acts as a precursor to give the coordinative unsaturated active catalytic species ‘ $\text{Mo}(\text{CO})_3$ ’ [1,4,5]:



The existence of $(\text{Ar})\text{Mo}(\text{CO})_3$ complexes is well known in literature. If $\text{Mo}(\text{CO})_6$ is heated in the presence of aromatic solvents $(\text{Ar})\text{Mo}(\text{CO})_3$ complexes are formed in situ [6], although the formation of $(\text{C}_6\text{H}_5\text{OH})\text{Mo}(\text{CO})_3$ was not observed under these conditions. The large excess of phenol required in the $\text{Mo}(\text{CO})_6$ catalysed alkyne metathesis reactions were thought to ensure a significant concentration of

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(C₆H₅OH)Mo(CO)₃ rather than assisting in the removal of the alkyne from the initial molybdenum complex [5]. It was shown that Mo(CO)₆ is unreactive towards the alkyne metathesis reaction in toluene, but could be regenerated with the addition of an excess amount of phenol [2].

A second theory suggested that phenol weakens the triple bond character of the alkyne substrate through intermolecular hydrogen bonding, causing the alkyne to be more reactive, i.e., similarly to the activity of an alkene [7]. It, furthermore, induces isomerisation of the metal-lacyclobutadiene intermediate in the metal carbyne mechanism generally accepted for alkyne metathesis. It is known that phenol forms hydrogen bonds with unsaturated organic compounds and that alkynes act as better proton acceptors for hydrogen bonds than alkenes and allenes [8]. It is also known that internal alkynes are more basic than terminal alkynes.

In a third theory it was suggested that phenol acts as a proton donor in a metal carbene mechanism proposed for alkyne metathesis to yield metallacyclobutane cations as intermediates [9]. These cations decompose further to yield metathesis and addition products. The metal carbene mechanism was proposed as a result of studies with the O₂Mo(acac)₂/(C₂H₅)₃Al/C₆H₅OH/4-nonyne catalytic system at 0°C [9].

In our view the above-mentioned theories should not necessarily be seen contradictory to one another but rather supplementary.

The Mo(CO)₆/C₆H₅OH catalytic system also catalyses the polymerisation of several other alkynes, i.e., phenylacetylene, 1-hexyne and 2-hexyne [10]. Small amounts of cyclotrimers and addition products were observed under certain conditions [10]. Only polymerisation was observed in the case of phenylacetylene and this reaction was studied more extensively in a previous study [11]. An excess amount of phenol (C₆H₅OH/Mo molar ratio ≥ 100) and high reaction temperatures (> 110°C) were required for optimum polymerisation conditions [12].

Both a metal carbene and a metal carbyne mechanism were proposed for the metathesis

and polymerisation reactions of alkynes in the presence of metathesis catalysts. Although the mechanism for alkyne metathesis has not yet been fully clarified, the metal carbyne mechanism is generally supported [3], while a metal carbene mechanism is supported for the metathesis polymerisation of alkynes [13].

In this paper the Mo(CO)₆/C₆H₅OH catalysed reactions of phenylacetylene and other alkynes were investigated further in an attempt to clarify the role of phenol in these reactions.

2. Experimental

The phenolic compounds, benzoic acid, salicylic acid, methanol (supplied by Holpro), molybdenum hexacarbonyl, and alkynes (supplied by Aldrich) were used as received. All the solvents (supplied by Merck) were dried using standard procedures.

The polymerisation procedure was performed under a dry nitrogen atmosphere in a closed glass reactor. The glass reactor with Mininert valve (Supelco) was placed in a glove bag in a nitrogen atmosphere and the catalyst Mo(CO)₆ (5 × 10⁻⁵ mol) and the phenolic or related cocatalyst added to the reactor. Following this the solvent (2 cm³) and alkyne were added each with a gastight syringe. The reactor was then placed in a heating block at 120°C. Chlorobenzene was used as solvent except during the investigation on the influence of solvent polarity on the polymerisation of phenylacetylene. Molar ratios of cocatalyst/Mo = 100 and alkyne/Mo = 100 were used unless otherwise specified. Monomer consumption was determined by gas chromatography. In general, a gradual change in the colour of the reaction mixture from yellow to yellow-brown was observed. The reaction mixture was kept at 120°C until completion of the reaction as determined by gas chromatography, after which it was cooled. Any polymer formed was precipitated in methanol (10 cm³), filtered off, washed with methanol and dried to constant weight.

Gas chromatographic analyses were performed on a Varian Aerograph series 2400 gas chromatograph (3 m × 3.2 mm stainless steel column with 10% OV 101 on Supelcoport; isothermal runs at 120°C; 25 cm³ min⁻¹ nitrogen carrier gas; flame ionisation detector).

3. Results and discussions

In a previous study we reported that the phenol content influenced the polymerisation of phenylacetylene in the presence of the Mo(CO)₆/C₆H₅OH catalytic system at 120°C [11,12]. For optimum results in terms of reaction rate, polymer yield and relative molecular weight of a C₆H₅OH/Mo molar ratio ≥ 100 is needed (Fig. 1). It is noteworthy that Mo(CO)₆ is active even in the absence of phenol (polymer yield of about 40% after 12 h), albeit at a slower rate. This is contrary to what was found in the case of the alkyne metathesis reaction where Mo(CO)₆ was inactive in the absence of phenol [2].

In an attempt to determine whether the relative acidity of phenol plays a role in the activity of the Mo(CO)₆/C₆H₅OH catalysed polymerisation of phenylacetylene, various phenolic and related compounds with different pK_a values

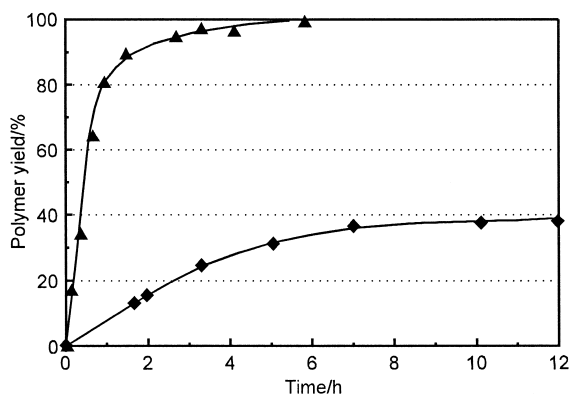


Fig. 1. Influence of the C₆H₅OH/Mo molar ratio on the Mo(CO)₆/C₆H₅OH catalysed polymerisation of C₆H₅C≡CH at 120°C. [(▲) 100; (◆) 0].

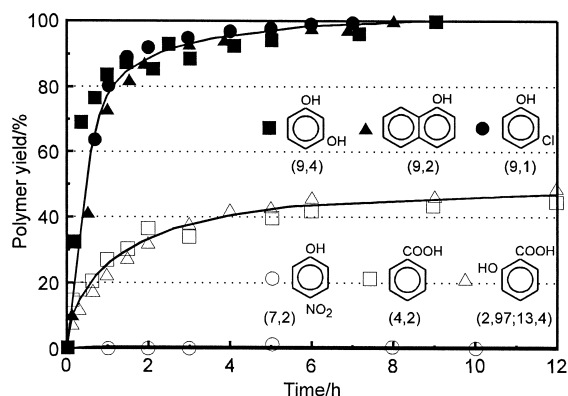


Fig. 2. Influence of phenolic compounds and benzoic acid on the Mo(CO)₆/C₆H₅OH catalysed polymerisation of C₆H₅C≡CH at 120°C (pK_a values are given in brackets).

were investigated. These results are illustrated in Fig. 2.

If these results are compared to the results in Fig. 1 it is obvious that similar results as with phenol (pK_a = 9.9) are obtained with resorcinol (pK_a = 9.4), 1-naphthol (pK_a = 9.2) and *m*-chlorophenol (pK_a = 9.1). From this it seems as if an increase in the proton donor capability of the phenol does not influence the polymerisation activity of the catalytic system. No polymer formed if *p*-nitrophenol (pK_a = 7.2) was used. The poisoning of the polymerisation reaction with *p*-nitrophenol can be attributed to the strong coordination properties of nitro groups to transition metal atoms rather than to the acidity of the compound because if nitrobenzene is used as solvent no polymer is formed either.

If salicylic acid (pK_a = 2.97 and 13.4) is used a polymer yield of only about 42% is observed after 12 h at a much slower rate (Fig. 2). This is similar to the results obtained in the absence of phenol in Fig. 1. It is also similar to the results obtained with benzoic acid (pK_a = 4.2). The lower polymerisation activity with salicylic acid and benzoic acid can be attributed to the higher proton donor properties of these compounds compared to that of the phenols and to the unavailability of a free hydroxyl group. The hydroxyl group in salicylic acid is

inter alia intramolecularly hydrogen bonded to the carbonyl oxygen of the acidic group on the *ortho* position, giving rise to the higher acidity and basicity of the acid and hydroxyl groups, respectively:



Although it may seem as if a free hydroxyl group is present in this hydrogen-bonded acid, the much lower pK_a value rather suggests an increase in the availability of the acid proton.

The above-mentioned results and discussion are confirmed by an investigation into the influence of solvent polarity on the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ catalysed polymerisation of phenylacetylene at 120°C (Fig. 3). The normalised E_τ values of solvent polarity according to Reichardt [14] were used to compare the different solvents and the values are summarised in Table 1.

The solvent polarity has a drastic influence on the reaction rate, as well as the polymer yield, of the polymerisation of phenylacetylene i.e., the more polar the solvent the less active is the catalytic system. In water similar results are obtained as in the absence of phenol (Fig. 1),

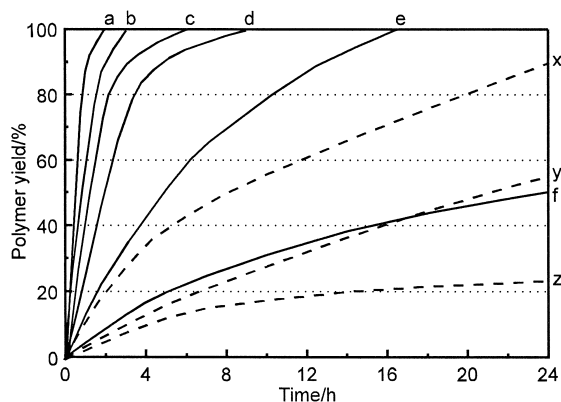


Fig. 3. Influence of the solvent polarity on the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ catalysed polymerisation of $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ at 120°C . [(a) $n\text{-C}_6\text{H}_{14}$, CCl_4 ; (b) C_6H_6 ; (c) $\text{C}_6\text{H}_5\text{Cl}$; (d) CHCl_3 ; (e) CH_3CN ; (f) H_2O ; (x) dioxane; (y) THF; (z) pyridine].


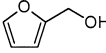
Table 1
Solvent polarity values according to Reichardt [14]

Solvent	E_τ^N value
<i>n</i> -Hexane	0.009
Carbon tetrachloride	0.052
Benzene	0.111
Chlorobenzene	0.188
Chloroform	0.259
Acetonitrile	0.460
Water	1.000
Dioxane	0.164
THF	0.207
Pyridine	0.302

and when salicylic acid and benzoic acid are used (Fig. 2). The influence of the solvent can also be related to the proton donor capability of phenol if it is envisaged that the proton donor capability of phenol increases with an increase in solvent polarity. Pyridine, THF and dioxane generally fit this picture although the lower activity of the catalytic system in these solvents may be attributed to a larger coordination effect of the solvent towards the metal atom of the catalyst. It does not seem as if the solvent structure as such influences the reactivity of the catalytic system.

Aliphatic and heterocyclic alcohols were also investigated as cocatalysts in the $\text{Mo}(\text{CO})_6$ catalysed polymerisation of phenylacetylene in chlorobenzene at 120°C (Table 2). The aliphatic alcohols CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $n\text{-C}_4\text{H}_9\text{OH}$ and

Table 2
Aliphatic and heterocyclic alcohols as cocatalysts in the $\text{Mo}(\text{CO})_6$ catalysed polymerisation of $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ at 120°C ($t = 6$ h)

	Polymer yield/% ^a
MeOH	7,8
EtOH	2,9
Bu ⁿ OH	3,0
	7,2
	35,5

^aPolymer yield was determined gravimetrically.

cyclohexanol are not nearly as effective as the phenolic compounds (polymer yields < 10% compared to 100% with phenolic compounds), they are even less active than $\text{Mo}(\text{CO})_6$ alone (Fig. 1). The inability of these compounds to activate the catalytic system for alkyne polymerisation can be attributed to the much higher basicity (and thus a lower hydrogen bonding capability) of these compounds relative to phenol.

An interesting result was obtained with furfuryl alcohol that has physical properties similar to that of phenol. Although the polymer yield is low this compound may be of value owing to the fact that it is a liquid (easier handling) and it is readily available as a by-product in the sugar industry. It is currently under further investigation. It is also noteworthy that the colour of the methanol insoluble polymers obtained with the aliphatic alcohols differs from those obtained from phenol (dark yellow to black compared to light yellow [11]).

Finally, some results obtained previously with different alkynes [10,15] are compared with those obtained with phenylacetylene and 1-phenylpropyne in the presence of the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ catalytic system at 120°C in Table 3.

A general trend can be observed from these results, i.e., terminal alkynes only polymerise in the presence of the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ catalytic system while internal alkynes undergo metathesis and/or polymerisation. From these results and if the metathesis results from literature [3] concerning the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ cat-

alytic system is inspected closely, it seems as if the bulkiness of the alkyl groups determines whether internal alkynes will metathesize only or polymerise as well. The influence of the structure of alkynes on the reactions of the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ catalytic system is currently under investigation.

4. Conclusions

Depending on a number of factors three reactions of alkynes are possible in the presence of the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ catalytic system at elevated temperatures, i.e., polymerisation, metathesis and addition of the phenol to the alkyne [10]. Of these the most effective is the polymerisation reaction. The optimum conditions (currently a $\text{C}_6\text{H}_5\text{OH}/\text{Mo}$ molar ratio ≥ 100 and reaction temperatures $> 110^\circ\text{C}$ [12]) for the conversion of phenylacetylene to polymers in the presence of the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ catalytic system can be extended to include phenolic compounds with unassociated hydroxyl groups and the use of a nonpolar solvent. The significance of the molar ratio of 100 is not yet fully understood, but it may be a further indication that the phenol is hydrogen bonded to the alkyne (the alkyne/Mo molar ratio = 100). The results obtained in this study further support the theory that the most important function of $\text{C}_6\text{H}_5\text{OH}$ is probably to weaken the triple bond character of the alkyne through intermolecular hydrogen bonding with the alkyne [16]. This conclusion is supported by the isolation of $\text{Cl}^m\text{C}_6\text{H}_4\text{OH} \cdot \text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ adducts in a previous study [10]. The fact that the polymerisation of phenylacetylene takes place even in the absence of phenol can be attributed to the intermolecular hydrogen bonding capability of terminal alkynes with the triple bond of a second alkyne molecule [17]. Phenylacetylene fulfils the role of phenol in this instance. In the case of internal alkynes hydrogen bonding between alkynes are not possible, thus no metathesis is

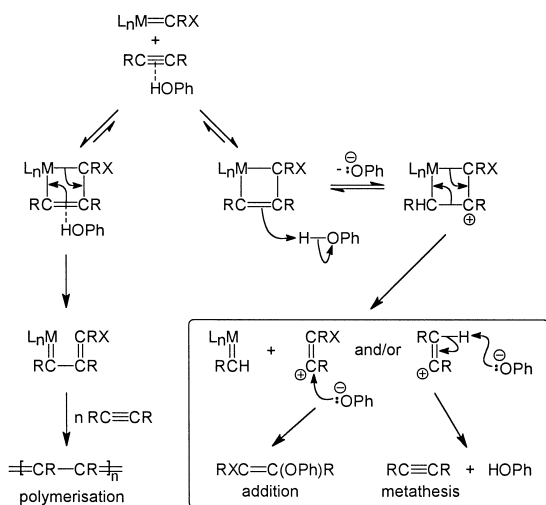
Table 3
Results obtained with different alkynes in the presence of the $\text{Mo}(\text{CO})_6/\text{C}_6\text{H}_5\text{OH}$ catalytic system at 120°C

Alkyne	Polymerisation (%)	Metathesis (%)
1-Phenylpropyne	0	20
2-Hexyne	26	10
1-Hexyne	100	0
Phenylacetylene	100	0
1,7-Octadiyne	100	0

observed in the absence of phenol. An increase in the polarity of the solvent increases the proton donor capabilities of phenol thus decreasing the hydrogen bonding capabilities of phenol with phenylacetylene, which then deactivates the catalytic system most probably through protonation.

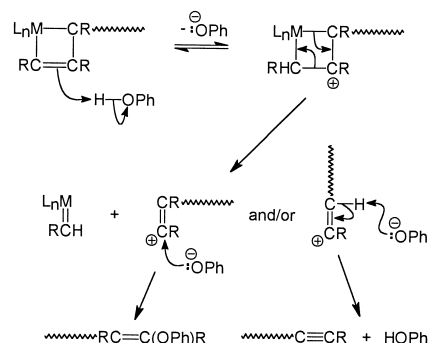
No evidence was found in literature or in this study for the formation of a $(C_6H_5OH)Mo(CO)_3$ complex under conditions typical of this study, although such a possibility cannot be ruled out entirely.

The observed reactions most probably follow a metal carbene mechanism similar to the mechanisms proposed by Masuda and Higashimura [13] for alkyne polymerisation and Vosloo and du Plessis [12] for alkyne metathesis:



A metal carbene mechanism seems evident because of inter alia the following reasons: (a) the simultaneous occurrence of metathesis and polymerisation if 2-hexyne is added to the $Mo(CO)_6/C_6H_5OH$ catalytic system, and (b) alkene metathesis products were observed in a preliminary study when 1-octene was added to the $Mo(CO)_6/C_6H_5OH/C_6H_5Cl/C_6H_5C\equiv CH$ reaction mixture at $120^\circ C$, 1 h after the polymerisation reaction commenced.

Termination of the polymerisation reaction is also possible via the metallacyclobutene–metallacyclobutane cation conversion:



The similar mechanisms for the addition and metathesis reactions and the termination reaction can be attributed to the bulkiness of the groups involved because metathesis is only observed when bulky groups are present in the internal alkyne molecule.

That phenol plays an important role in the termination step is supported by the fact that the C_6H_5OH/Mo molar ratio does not only influence the activity of the catalytic system but also the molecular mass of the polyphenylacetylene [12]. This rationale favours the regeneration of phenol in the termination step to form polymers with alkyne end groups. Up to this stage alkyne end groups were not yet observed in the spectra [11] of these polymers and it may be due to very low concentrations of such groups in the polymer chains which are of considerable length [11,12]. A termination route where the end groups are alkene groups is also possible, but the shown routes are preferred because of the observed formation of the addition adducts [10].

Acknowledgements

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